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A Method of Calculating Cross Sections for Molecular Collisions

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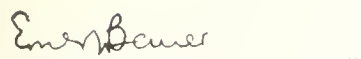

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Abstract

The calculation of slow inelastic collisions of molecules, such as occur in chemical reactions, shows an interesting combination of classical and quantum mechanical features. The de Broglie wavelength is small compared to the range of the intermolecular potential, so that there exists a relatively well-defined quasi-classical orbit; but in some cases the coupling constant is small compared with unity, and this gives the problem certain quantum mechanical characteristics. On account of the condition relating to the de Broglie wavelength, a calculation of the total collision cross section requires the knowledge of the partial waves for a large number of values of the angular momentum $\ell\hbar$.

A method is devised to suit these different features. The WKB method, with a quasi-classical amplitude and a quantum mechanical phase for the wave function, is well suited for our problem. We also use the concept of an impact parameter b rather than the orbital quantum number ℓ: this is well suited for describing a quasi-classical orbit, and hence for calculating the total cross section in a case like the present one. As an example of the method, the cross section for excitation of the first vibrational state of a hydrogen molecule resulting from collision with another hydrogen molecule is calculated.

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1. Introduction

The aim of this work is to calculate the cross section for the excitation of molecular vibrations by collisions between a molecule and another molecule or an atom, at energies so low that the translational and vibrational energies are of the same order of magnitude. Processes of this kind are basic to many gas phase chemical reactions [1], [2] and also to phenomena such as the "vibrational relaxation" that has been suggested as a mechanism for the large absorption of high-frequency sound in gases [3].

Numerous quantum mechanical calculations of this kind of process have been made [4] - [8] and the correct order of magnitude for the cross section has been obtained. The problem of measuring cross sections for this kind of process experimentally is a very difficult one because the energy of translation is low, so that no detailed numerical data such as angular distributions can be expected. From a theoretical standpoint there are serious difficulties connected with the form of the intermolecular potential, and also with the mathematical treatment of the translational motion.

On account of the complexity of the problem, which arises from the large number of electrons and nuclei involved, it has not been possible to give convincing quantitative calculations of the intermolecular (van der Waals) potential for any but the very simplest systems [9]. The quantitative knowledge that is available on the van der Waals potential of most molecules [10] has been derived from a knowledge of macroscopic properties of the gas, such as the viscosity and the second virial coefficient, by means of various statistical mechanical models. From a logical standpoint this is a very unsatisfactory method of proceeding, both because many different models could give the same values for the macroscopic constants, and also, more specifically, because viscosity and other such properties

depend on the behavior of a gas in near-equilibrium, when the molecules are generally far apart, and in studying collisions, we are interested in the characteristics of the intermolecular potential at the opposite extreme, namely when the molecules are in close proximity*. In the present work we shall make heuristic assumptions regarding the form of the potential, similar to those that have been made previously [6]. As far as this aspect of the problem is concerned, it seems that at present one cannot hope for any radically improved results, although undoubtedly more extensive calculations along the established lines [9] will be carried out. However, with a reasonably reliable and rapid method of calculation it might be possible to consider a program of determining the potential from the value of the cross section, by varying the parameters involved in the potential in a systematic way, or conceivably even by more sophisticated methods.

The central aim of this work is the presentation of a relatively rapid method for calculating the cross section for slow inelastic collisions in which the Born approximation is not valid and where it is not possible to restrict oneself to the calculation of a relatively small number of partial waves.

The problem is this. We wish to make a perturbation calculation of the cross section for the transfer of energy between two degrees of freedom**.

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* A typical example is the Lennard-Jones 6-12 form $(a/r^{12} - b/r^{6})$ normally used for the van der Waals potential; while this is adequate at large intermolecular separations and does reproduce the known minimum in the potential, it is entirely unsatisfactory at small separations, where the potential is known to behave [6] like $1/r$ rather than like $1/r^{12}$.

** The "perturbation" character is inherent not only in the present (and all previous) methods of calculation, but even in the qualitative description of the system in terms of separate degrees of freedom. The underlying reason for this arises from the fact that it is in general impossible to solve problems involving several degrees of freedom exactly, such as even the classical three-body problem.

The Hamiltonian H consists of an unperturbed part

$$H^o = T^o + V^o$$

(T = kinetic energy; V = potential energy), and a small perturbation V' that provides a coupling between the different degrees of freedom*.

The degrees of freedom in our system are translational ("external") and internal. The internal motion in the present problem is vibrational, but one could equally well consider rotation. In any case, the internal motion is quite well understood, and will not be discussed here; the problem is to give a suitable treatment for the translational motion. The latter is characterized by a reduced mass M_e ("e" for "external"), an energy $E = \hbar^2 k^2/2M_e$, and an impact parameter b related to the angular momentum $\hbar\ell$ by the relation

$$\hbar\ell = \hbar k b \quad . \tag{1}$$

The potential V^o is made up ot two parts, namely V_i^o, which determines the internal motion, and V_e^o, which acts on the translational degrees of freedom. The potential V_e^o has a definite range R, and the perturbation potential V' also has a definite range, $R' \gtrsim R$, in the translational coordinate.

The essential character of the translational motion is defined in terms of two conditions. First, the de Broglie wavelength $\lambda\!\!\!^{-} = 1/k$ is very much smaller

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* If we introduce the notation

$$a \ll^* b$$

for "a is very much less than b almost everywhere", then the perturbation approach will be valid if the condition

$$V' \ll^* H^o$$

is satisfied, and slow collisions may be defined by the condition

$$T^o \ll^* V^o \quad .$$

than R:

(2) $$\lambda\!\!\!^{-} = 1/k \ll R \ .$$

This condition arises from the large value of the particle mass M_e, which gives large values for k even for small energies E. The physical meaning of the condition (2) is that there exists an orbit for our colliding particles in something like the classical sense: there is a diffuseness in this orbit of order $\lambda\!\!\!^{-} = 1/k$, but this is small compared with the " natural length" R for the problem.

There is yet a second condition, concerning the magnitude of the momentum transferred in a collision in relation to the uncertainty principle. Roughly, we may say that the momentum transferred is given by the expression

(3) $$\delta p \sim \int \text{grad } V' \, dt \ ,$$

where the integration extends over the whole collision, so that

(3a) $$\delta p \sim \frac{V' R M_e}{Rhk} = \frac{V' M_e}{hk} \ .$$

We now ask: what is the order of magnitude of the expression*

(4) $$\delta p R / \hbar \sim V' R \, M_e / \hbar^2 \, k \ .$$

If the expression (4) is much larger than unity, then the effects of the uncertainty principle - or quantum mechanical effects generally - will be small, so that we may treat the translational motion classically. If (4) is very much less than unity, we must treat the translational motion in terms of quantum mechanics, even though the orbit may be well defined, in view of condition (2)**.

---

* For Coulomb scattering, $V' = Ze^2/r$, so that if we are willing to speak of a range R in this case, the expression (4) is just $Ze^2/\hbar v$.

** There is no inconsistency here, because (2) involves k and R, whereas (4) involves V', R, M_e, and k, so that (2) and (4) are essentailly different.

It turns out that in the present problem (4) is frequently small compared with unity (c.f. Table II), so that a strictly classical treatment of the translational motion[7] is not completely satisfactory.

The two conditions involving (2) and (4) are basic to the present problem. It is clear from (1) and (2) that one must consider values of the impact parameter $b \lesssim R$, and thus angular momenta $\ell\, h < \ell_1\, h$, where

$$\ell_1 = kR \gg 1 \,. \tag{5}$$

Actually $\ell_1 \sim 10 - 100$ in the present case (c.f Table II), and this determines the method of attack: basically we use perturbation theory[11], but in a different representation from that usually employed. Normally one would expand the solution in spherical harmonics of order $\ell\,(= 0,1,2,3,\ldots)$, solve the radial equation (an ordinary differential equation) for each value of ℓ, and then sum the contributions for all $\ell \lesssim \ell_1$ to give the total cross section. This procedure would clearly be exceedingly lengthy in the present case, and thus we use a wave function characterized by the impact parameter b rather than by ℓ; to obtain the total cross section, we integrate over all $b \lesssim R$.

Here we use the WKB method in an impact parameter formulation. The WKB method is essentailly an asymptotic expansion in powers of $\hbar$ (or $1/k$ or $1/M_e$) and involves a wave function of form $A\, e^{iS/\hbar}$, where $|A|^2$ is a density function, and S a phase. In view of condition (2), the density $|A|^2$ just follows the classical orbit, described by the impact parameter b, with the quantum width $\lambda\!\!\!^{-} = 1/k \ll R$; the phase S is a solution of the Hamilton-Jacobi equation of the problem.

2. Specifications of the problem

We consider a molecule AB colliding with an atom or molecule C. A,B, C are regarded as "particles" of respective masses M_A, M_B, M_C; each such

"particle" is essentially the nucleus with a given potential field determined by the orbital electrons, which themselves are not explicitly considered here. This "adiabatic" separation of the electronic from the nuclear motions is justified in the present problem because it follows from the low energies of the heavy-particle motions under discussion that the velocities of the heavy particles are several orders of magnitude smaller than the electronic velocities, so that there is practically no possibility of energy transference between electronic and nuclear (translational, rotational, vibrational) modes of motion.

In discussing total collision cross sections, it is convenient to eliminate the motion of the center of mass. Thus we use the following coordinates:

$$\begin{aligned} \underline{\rho} &= \underline{r}_{AB} \\ \underline{r} &= \underline{r}_C - (M_A \underline{r}_A + M_B \underline{r}_B)/(M_A + M_B) \\ \underline{R} &= (M_A \underline{r}_A + M_B \underline{r}_B + M_C \underline{r}_C)/(M_A + M_B + M_C) \ . \end{aligned} \tag{6}$$

Here $\underline{\rho}$ is the internuclear separation of the molecule AB and describes its internal motion (rotation, vibration); $\underline{r}$ is the coordinate of the incident particle C relative to the center of mass of the molecule AB and describes the translational motion. $\underline{R}$ is the coordinate of the center of mass of the system as a whole; it is irrelevant to the present discussion and will not be used explicitly here.

The reduced masses are

$$M_i = M_A M_B / (M_A + M_B), \text{ and } M_e = M_C(M_A + M_B) / (M_A + M_B + M_C) \ . \tag{7}$$

We shall consider the case when A = B, and C = AB; then

$$M_i = \frac{M_A}{2}, \quad \text{and} \quad M_e = M_A \ . \tag{7a}$$

We are concerned with a transition in which the system goes from one state O to another state f. Any given state j of the system as a whole can be characterized by specifying both the internal (vibrational and rotational) and

external (translational) motions; this may conveniently be done by giving the internal energy $\varepsilon_j = \hbar \omega_j$ for a pure vibration, and the momentum $\hbar \underline{k}_j$, which is related to the translational energy E_j by $E_j = \hbar^2 k_j^2 / 2M_e$. Then it is clear that if no rotational transitions occur between our states 0 and f, we have conservation of energy in the form

$$(8) \qquad \hbar (\omega_f - \omega_o) = (k_o^2 - k_f^2) \hbar^2 / 2M_e .$$

It should be noted that conservation of linear momentum is ensured automatically because we have eliminated the motion of the center of mass of the system as a whole; conservation of angular momentum will have to be considered separately (cf. Section 5).

In the present work we are concerned explicitly with a transition involving only translational and vibrational motion, and in particular the normal and first excited vibrational states of the molecule in question. The method can obviously be applied to other processes, such as the excitation of rotation by collisions, but at least for an initial discussion it is desirable to have the internal and external modes of motion as different in character as possible, because they are treated on a rather different basis.

3. The potential

We wish to express the potential energy of the system AB + C in terms of the coordinates $\underline{\rho}$, $\underline{r}$ in such a way that we may write*

$$(9) \qquad V = V(\underline{\rho}, \underline{r}) = V_i^o(\underline{\rho}, \underline{r}_o) + V_e^o(\underline{\rho}, \underline{r}) + V'(\underline{\rho} - \underline{\rho}_o, \underline{r}; \underline{\rho}_o) .$$

At this point we neglect any non-central characteristics of V and proceed as follows. Consider our three particles A, B, C to lie along a straight line, and assume that all interactions may be represented as those between two atoms. Then

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* For a symmetrical way of treating $\underline{\rho}$ and $\underline{r}$, cf. ref. [6] .

$$V = V(r_{AB}) + V(r_{CA}) \quad . \tag{10}$$

$V(r_{AB})$ is the internal potential energy of the AB-molecule, and thus its quantitative character is well known from spectroscopic evidence: we call it $V_i^o(\underline{\rho}, \underline{r}_o)$, since $\underline{\rho} = \underline{r}_{AB}$. For the external (van der Waals) potential between the atoms, i.e.,

$$V_e = V_e^o + V' = V(r_{BC}) + V(r_{CA}) \quad , \tag{11}$$

we substitute Morse expressions

$$V(x) = U_o\left[e^{-2a(x - x_o)} - e^{-a(x - x_o)}\right] \tag{12}$$

rather than the more conventional Lennard-Jones 6-12 form (see first footnote on p. 2).

We now take the case A = B, C = AB = A_2, with the three particles A, B, C in a straight line, so that

$$r_{BC} = r - \frac{\rho}{2} \; ; \quad r_{CA} = r + \frac{\rho}{2} \quad . \tag{6a}$$

Substituting (6a) and the form (12) for $V(r_{BC})$, $V(r_{CA})$ into (11), we finally get the result

$$V_e^o(\rho_o, r) = U_e^o\left[e^{-2a(r - d)} - e^{-a(r - d)}\right] \quad ,$$

$$U_e^o = U_o \frac{2\left[\cosh(a\rho_o/2)\right]^2}{\cosh(a\rho_o)} \; ; \quad d = x_o + \left(\frac{1}{a}\right) \log\left[\frac{\cosh(a\rho_o)}{\cosh(a\rho_o/2)}\right] , \tag{13}$$

and

$$V'(d\rho, r) = U' a\, d\, \rho\left[e^{-2a(r - z_o)} - e^{-a(r - z_o)}\right] \quad ,$$

$$U' = U_o \frac{\left[\sinh(a\rho_o/2)\right]^2}{2\sinh(a\rho_o)} \; ; \quad z_o = x_o + \left(\frac{1}{a}\right) \log\left[\frac{2\sinh(a\rho_o)}{\sinh(a\rho_o/2)}\right] . \tag{14}$$

We still have the problem of determining the correct numerical values of the constants U_o, a, ρ_o, x_o. These must be chosen to give the correct equilibrium nuclear separation ρ_o, and also the correct van der Waals potential V_e^o. The numerical values chosen for the case of two hydrogen molecules colliding are listed in Table I. They are essentially the values of Evett and Margenau [9], which were

found to agree very well with the empirical value obtained from viscosity and second virial coefficients [10].

Table I. The van der Waals potential V_e for two hydrogen molecules [9]

cf. equations (12), (13), (14).

$U_e^o = 4.18 \times 10^{-4} \; e^2/a_o$

$a = 0.916 \; a_o$

$\rho_o = 1.40 \; a_o$

$d = 5.67 \; a_o$

$U' a\rho_{01} = 5.86 \times 10^{-6} \; e^2/a_o$

$z_o = 6.87 \; a_o$

N.B.: (i) The data for V_e^o are reasonably satisfactory numerically.

(ii) V' is not so certain, but we require

(iia) $z_o - d > \lambda\!\!\!^{-}$ (cf. second footnote, p. 14)

(iib) $V' \ll V_e^o$, rather than $V' \ll^* V_e^o$.

It must be stressed that the present discussion of the potential is far from being self-consistent or satisfactory. There is a lack of consistency in the fact that the internal potential $V_i^o(\underline{\rho}, \underline{r}_o) = V(r_{AB})$ and the external potential $V_e = V_e^o + V'$ are treated in completely different ways. We see empirically that one cannot use the expression (12) with the same set of constants U_o, a, x_o, ρ_o for both V_i^o and V_e^o, because the numerical values of the two potentials are so different: in particular, the well depth in V_i is of order 4.5 ev for hydrogen, and 0.01 ev in the case of V_e. This quantitative difference is entirely understandable in terms of the distortion of the "electron cloud" of the molecule at close nuclear separations and the attendant complications, but it does show clearly the heuristic character of the derivation of V_e^o and V'. The numerical values of V_e^o used here are reasonably satisfactory, but it is clear that the numerical values used for V', which depend on the differentiation of the function V_e^o, cannot be

expected to be accurate.

However, since our purpose is to derive a method for calculating cross sections, it has been necessary only to find a potential which is sufficiently plausible in its qualitative and semi-quantitative behavior for the numerical values of the cross sections resulting from the calculations to have meaning. Any refinements will be left for future work.

4. The perturbation scheme

Disregarding the motion of the center of mass of the system, we may write the total Hamiltonian H as

$$H = H(\underline{\rho}, \underline{r}) = T_i(\underline{\rho}) + T_e(\underline{r}) + V_i^o(\underline{\rho}) + V_e^o(\underline{r}) + V'(\underline{\rho}, \underline{r}), \tag{15}$$

where the kinetic energy terms T are given by the usual expressions

$$T_i(\underline{\rho}) = -(\hbar^2 / 2M_i) \triangle_{\underline{\rho}} \quad ; \quad T_e(\underline{r}) = -(\hbar^2 / 2M_e) \triangle_{\underline{r}}, \tag{16}$$

and the potential energy terms V have the values of Section 3 and Table I.

We treat V' as a small perturbation, and describe eigenstates of the unperturbed system as

$$\phi_j(\rho)\ \chi_j(\underline{r}),$$

where $\phi_j(\rho)$, $\chi_j(\underline{r})$ are, respectively, solutions of

$$\left[T_i(\underline{\rho}) + V_i^o(\underline{\rho}) - \hbar\omega_j\right] \phi_j(\underline{\rho}) = 0 \tag{17}$$

and

$$\left[T_e(\underline{r}) + V_e^o(\underline{r}) - \hbar^2 k_j^{\,2} / 2M_e\right] \chi_j(\underline{r}) = 0. \tag{18}$$

In the present work we treat the $\phi_j(\underline{\rho})$ as known functions: the problem is to find suitable functions $\chi_j(\underline{r})$ by solving equation (18), and in particular to

find an expression for the transition matrix element $(f|V'|0)$.

5. The orbit

On account of condition (2), we can speak of an orbit which follows the classical path, but has a width λ arising from the uncertainty principle. Accordingly, we consider first the classical motion of a particle C moving with momentum $\hbar\underline{k}_o$ towards the molecule AB, exciting this molecule into a vibrational state f, and then leaving with momentum $\hbar\underline{k}_f$. The initial orbit of C is asymptotically a straight line, and the length of the perpendicular from the center of mass of the molecule AB onto the continuation of this straight line is known as the "impact parameter" b_o of the initial orbit. We define similarly an impact parameter b_f for the final orbit (cf. Fig. 1).

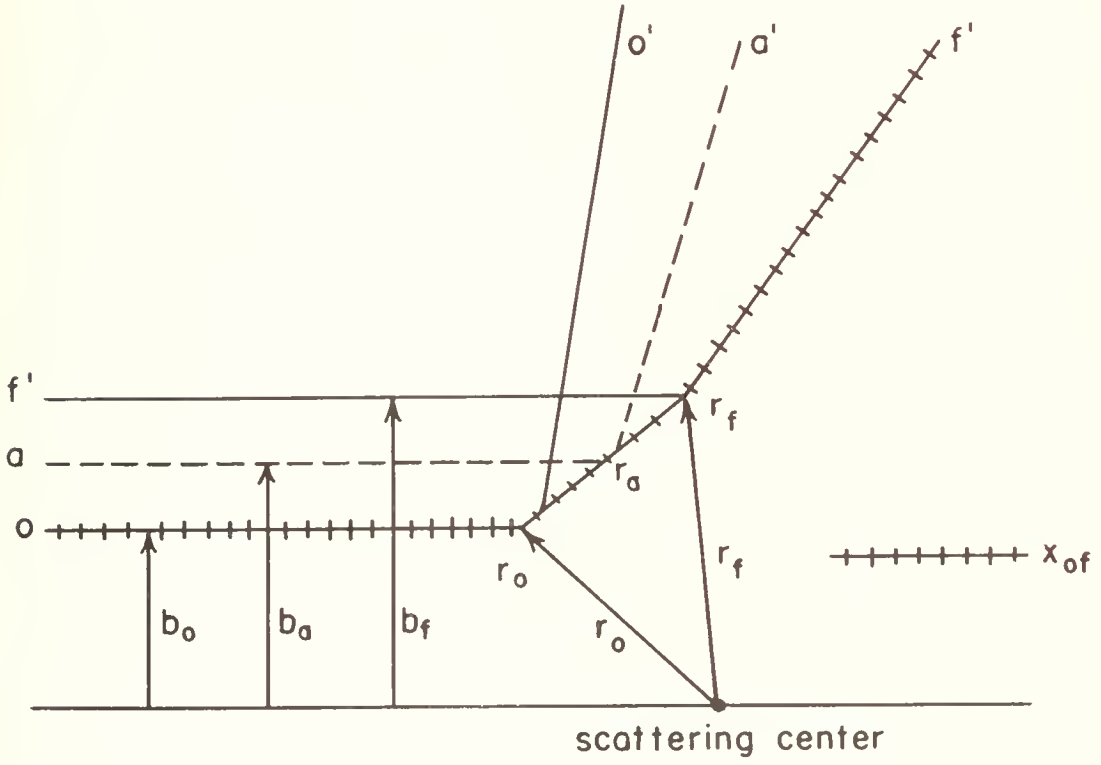

Figure 1. The orbit.

We now ask the following question: given the asymptotic forms of the initial and final asymptotic orbit, what is the actual orbit which links them? For definiteness, we suppose

(i) that the scattering potential is central: this enables us to locate the classical motion in a plane;

(ii) that no rotational motion is excited, so that angular momentum is conserved. The condition for conservation of angular momentum is*

$$\hbar k_o b_o = \hbar k_f b_f - \hbar \ell \quad ; \tag{19}$$

(iii) that the potential $V_e^o(\underline{r})$ which determines the orbit has a short range: again, this assumption is convenient but, like the other conditions, not necessary in principle.

It is evident from physical considerations that in the classical case the actual orbit passes continuously through all classical orbits a that satisfy

$$\hbar k_a b_a = \hbar k_o b_o = \hbar k_f b_f \tag{20}$$

and

$$k_f^2 \leq k_a^2 \leq k_o^2 \quad . \tag{21}$$

If the potential V_e^o is of sufficiently short range, the orbit will in fact pass through the locus of the turning points $\underline{r}_a$ of all orbits a satisfying the conditions (20) and (21). This situation is illustrated in Fig. 1.

The orbit $0\ \underline{r}_o\ \underline{r}_a\ \underline{r}_f\ f$ shown in Fig. 1 is the classical one, $\underline{x}_{of}$. We consider our particle as moving along it with appropriate speed, and producing a potential $V'(\rho\ ,\ \underline{x}_{of}(t)\ )$ at the position of the molecule AB. This potential $V' = V'(\rho\ ,t)$ now induces transitions in the internal state of AB. Explicitly,

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* If J quanta of angular momentum are excited, we have

$$\hbar k_o b_o - \hbar k_f b_f - \hbar J$$

instead of (19), but this does not change the method fundamentally.

in the classical limit for the expression (4) the potential inducing transitions in AB is

$$(22) \qquad V'(\rho, \underline{x}_{of}) = \int d^3\underline{r}\ \delta(\underline{r} - \underline{x}_{of})\ V'(\rho, \underline{r}) ,$$

where $V'(\rho, \underline{x}_{of})$ represents a function of ρ and of the time t, since the speed of particle C in the orbit $\underline{x}_{of}$ is known*.

In the case under consideration here, we may still speak of an orbit, but it is now blurred rather than sharp as in the classical case just discussed. We specify our set of states precisely as in the classical case, except that now we cannot give a sharp value for the impact parameter b_j, but can only specify it to within the quantum uncertainty:

$$(23) \qquad \delta b_j \sim \lambda\!\!\!^{-}_j = 1/k_j \qquad (j = 0,a,f) .$$

We shall discuss wave functions which follow the classical orbits but have the quantum width δb_j. These functions will be determined by the WKB method, as outlined in the next section.

When a particle moves in a short range potential V_e^o, its orbit can be split up into the asymptotic portions $0\ \underline{r}_o$ and $\underline{r}_f\ f$ beyond the turning points of the initial and final orbits, and into the region $\underline{r}_o\ \underline{r}_a\ \underline{r}_f$ between these turning points (cf. Fig. 1). It is this latter region between the turning points that is important in our problem on account of the short range of the perturbation potential V'.

The turning points of the orbits are readily characterized by the classical distances of closest approach, r_j. These are the appropriate solutions

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* That is, the effect of the particle C on the molecule AB has been reduced to that of a given field function depending only on the time, and not on any dynamic variable of the relative motion.

of*

$$E_j(1 - b_j^2 / r_j^2) - V_e^o(r_j) = 0 \quad . \tag{24}$$

At the point of closest approach the momentum $\hbar k_j$ is diminished to a value $\hbar q_j(r_j)$ given by

$$q_j(r_j) = k_j b_j / r_j \quad . \tag{25}$$

It should be noted here that for a quantum mechanical orbit characterized by k_j, b_j, r_j, the actual particle density $|\chi_j|^2$ has its maximum not at the point $\underline{r}_j$, but at a point r_j' at a distance $r_j + \lambda\!\!\!^{-}_j$ from the molecule AB **. Accordingly, in evaluating matrix elements, the perturbation potential and the effective wave numbers will be evaluated at this point $\underline{r}_j'$ rather than at $\underline{r}_j$.

6. Application of the WKB method [12]

A simple and convenient expression for the translational wave function $\chi_j(\underline{r})$ is given by the WKB solution of the wave equation (18) , namely

$$\chi_j(\underline{r}) = A_j(\underline{r}) \exp\left\{ i S_j(\underline{r}) / \hbar \right\}, \tag{26}$$

where the action function $S_j(\underline{r})$ satisfies the Hamilton-Jacobi equation corresponding

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* The physical meaning of equation (24) is that the point of closest approach is characterized by the condition that the potential energy, increasing with decreasing separation r , has diminished the total kinetic energy until its net value, $E_j - V_e^o(r)$, is just balanced by the energy arising from the rotational motion connected with the angular momentum $\hbar = \hbar k_j b_j$, namely $\hbar^2 k_j^2 b_j^2 / 2 M_e r^2$., or $\hbar^2 \ell(\ell+1) / 2 M_e r^2$.

** This is due to the behavior of the wave function near a turning point. For one-dimensional examples, cf. Reference [5a], Section VI, or Reference [6], Fig. 3.

to (18), namely

$$(27) \qquad (\text{grad } S_j)^2 + 2 M_e V_e^o(\underline{r}) = \hbar^2 k_j^2 \ ,$$

and $|A_j|^2$ satisfies the equation of conservation of particle flux:

$$(28) \qquad \text{div} \left[\left\{ \hbar \, \underline{q}_j(\underline{r})/M_e \right\} |A_j|^2 \right] = 0 \ ;$$

here $\underline{q}_j(\underline{r})$ is the effective wave number defined in equation (29) below.

We can assume that the solution of our problem is always a wave function of the form (26). If we then make asymptotic expansions of S_j and A_j in powers of $\hbar$ or $1/k_j$ or $1/M_e$, the leading terms for S_j and A_j are given respectively by (27) and (28).

The action function $S_j(\underline{r})$ is given by an expression of the form

$$(29) \qquad S_j(\underline{r}) = \int d\underline{r} \cdot \underline{q}_j(\underline{r}) \ ,$$

where

$$(30) \qquad q_j(\underline{r})^2 = k_j^2 - (2 M_e/\hbar^2) V_e^o(\underline{r}) \ .$$

We choose the density function $A_j(\underline{r})$ to satisfy the following conditions:

(i) $\chi_j(\underline{r})$ shall follow the classical orbit, but with a width $\delta b_j = 1/k_j$.

(ii) $\chi_j(\underline{r})$ shall be normalized per unit energy range, and also with respect to impact parameter (i.e., angular momentum). A detailed discussion of the normalization is given in Appendix A; here we merely quote the result:

$$(31)\qquad |A_j(\underline{r})|^2 = \begin{cases} 2\,M_e \Big/ \left\{ \hbar^2\, \pi\, q_j(\underline{r})\, 2\pi\, b_j\, \delta\, b_j \right\} & \text{along the classical orbit } \left(b_j \pm \frac{\delta b_j}{2}\right) \\ 0 & \text{off the orbit.} \end{cases}$$

7. Perturbation matrix elements

Consider the internal (vibrational) state of the molecule AB. In a collision this is perturbed by a potential arising from the passage of the third particle C. In particular, the perturbation potential $V'_{of}(\underline{\rho})$ acting on the $\underline{\rho}$-coordinate is

$$(32)\qquad V'_{of}(\underline{\rho}) = d^3\underline{r}\; V'(\underline{\rho}, \underline{r}) \begin{cases} \delta(\underline{r} - \underline{x}_{of}) & \text{classical case, C.} \\ \chi_f^*\ \chi_o & \text{quantum mechanical case Q.} \end{cases}$$

$\underline{x}_{of}$ is the classical particle orbit, here interpreted as a function of time alone (see footnote on page 13). In our problem we know that the actual orbit follows the classical orbit $\underline{x}_{of}$, but has a width λ. In view of the form of the wave function χ (= A exp(iS/h)), we shall take for the total matrix element, i.e., for

$$(33)\qquad (f|V'|0) = \int d^3\underline{\rho}\; \phi_f^*\, \phi_o\, V'_{of}(\underline{\rho}),$$

the expression

$$(34)\qquad (f|V'|0) = \iint d^3\underline{\rho}\; d^3\underline{r}\; \phi_f^*\, \phi_o\, V'(\underline{\rho},\underline{r})\, A_f^*(r)\, A_o(\underline{r})\, X$$

where X = 1 in the case C ($\delta\, p\, R/\hbar \gg 1$), and $X = \exp\left(i(S_o - S_f)/\hbar\right)$ in the case Q ($\delta\, p\, R/\hbar \ll 1$). The present calculations have been carried out for both the cases C and Q.

We may simplify equation (34) by means of the following considerations:

(i) from the discussion in Section 5, we know that the volume integration over $d^3\underline{r}$ may be reduced to a line integration over $d\underline{x}_{of}$, evaluated with the

appropriate width $\delta b_j \sim \lambda_j$. This is the fundamental simplification of the present method. In addition there are the following simplifications of a more technical nature, arising from the character of the phase S_j of the wave function.

(ii) On account of the short range of the potential V', the line integration over $d\underline{x}_{of}$ does not have to be taken over the whole orbit, but only over a finite and rather short portion near the turning points. In particular, we shall take the integral only over the non-asymptotic portion of the orbit, which is roughly the region $\underline{r}_o\ \underline{r}_a\ \underline{r}_f$ of Fig. 1. The line element in this " effective region of interaction" is denoted by dx, and because the whole region is relatively short, we shall replace the expression (29) for S_j by the simpler form

$$S_j(\underline{x}) = \underline{q}_j(\underline{x}) \cdot \underline{x} \ . \tag{35}$$

We shall make yet a further simplification here, and write

$$\left\{ S_o(\underline{x}) - S_f(\underline{x}) \right\} \hbar^{-1} = \left\{ \underline{q}_o(\underline{r}_o') - \underline{q}_f(\underline{r}_f') \right\} , \qquad \underline{x} = q_{of}' \, x \ , \tag{36}$$

bearing in mind the fact, discussed in Section 5, that the particle density has its maximum at a point $r_j' = r_j + 1/k_j$ in distance from the scattering center.

Let the length of this 'effective region of interaction' be x_m. Then it turns out that the relation

$$q_{of}' \, x_m \gg 2\pi \tag{37}$$

is satisfied, so that the exponential phase in the wave function, $\exp\left[i(S_o - S_f)/\hbar\right]$, makes a relatively large number of oscillations over the interaction region. On account of this, one may neglect other, less rapid, variations in functional behavior inside the integral over dx. In particular:

(iii) The amplitude function $A_j(\underline{r})$ is not a very rapidly varying function of $\underline{r}$ along the orbit, and thus we may replace it by its value at the point $\underline{r}_j'$, namely $A_j(\underline{r}_j')$.

(iv) Similarly, $V'(\underline{x})$ is a slowly varying function (although not in general as slowly varying as $A_j(\underline{x})$), and thus we shall replace the function $V'(\underline{\rho},\underline{x})$ inside the $\underline{x}$-integral by $\left[V'(\underline{\rho}, \underline{r}_o')\ V'(\underline{\rho},\underline{r}_f')\right]^{1/2}$ outside this integral.

Combining all these approximations, we arrive at the expression

$$(f|V'|0) = \int d^3\,\underline{\rho}\ \phi_f^*(\underline{\rho})\ \phi_o(\underline{\rho})\ \sqrt{V'(\underline{\rho}, \underline{r}_o')\ V'(\underline{\rho}, \underline{r}_f')}\quad A_f^*(\underline{r}_f')\ A_o(\underline{r}_o')\ .$$

$$(38)\qquad \times 2\pi \sqrt{b_o\ \delta b_o\ b_f\ \delta b_f} \begin{cases} x_m & \text{for case C} \\ \dfrac{2}{q_{of}'} \sin\left(\dfrac{q_{of}'}{2} x_m\right) & \text{for case Q,} \end{cases}$$

which may be simplified further by using the expression (31) for $A_j(\underline{r})$, and (14) for $V'(\underline{\rho},\underline{r})$.

8. The total cross section

Equation (38) gives the transition matrix element $(f|V'|0)$ for given wave numbers k_o, k_f as a function of the impact parameter. The formulation is of course inherently symmetrical both in b_o and in b_f, but for definiteness we shall express the cross section σ in terms of an integral over b_f, which is related to b_o by equation (19). We have

$$(39)\qquad \sigma_{of} = \int_0^\infty 2\pi\ b_f\ db_f\ |(f|V'|0)|^2\ ,$$

where $(f|V'|0)$ is taken as a function of b_f.

It is clear that (39) is to be considered as an approximation to the cross section calculated by means of

$$(40) \qquad \sigma'_{of} = \sum_{\ell=0}^{\infty} \frac{4\pi}{k_o k_f} (2\ell + 1) \left|(f|V'|0)\right|^2,$$

where now $(f|V'|0)$ is the conventional transition matrix element, regarded as a function of ℓ . One would expect the replacement of (40) by (39) to be satisfactory for $\ell >> 1$, where the step size $\delta\ell/\ell$ is small; in problems such as ours, the most important contribution to σ_{of} comes from relatively large ℓ (cf. Table II, and Fig.2) so that one may safely use (39) instead of (40).

Detailed comparisons of the partial cross sections $\sigma'_{of}(\ell)$ and $\sigma''_{of}(\ell)$ have been made for a number of values of ℓ and of the energy, and the orders of magnitude of the results of the two methods are in good agreement.

The actual calculations of the partial cross sections $\sigma'_{of}(\ell)$ shows clearly the usefulness of the present method of calculation. For a typical energy value, we have to consider some 60 phases. Suppose one calculates every third or every sixth phase; then one actually has to compute some 20 - 10 values of $\sigma'_{of}(\ell)$ for every value of the energy. It turns out in practice that each of these $\sigma'_{of}(\ell)$ requires approximately as much time in evaluation as does the total cross section σ''_{of} for one value of the energy.

The results for σ''_{of} as a function of energy in the C- and Q- limit of expression (4) are listed in Table II, and shown in Fig. 3. The character of the results is reasonable in both the energy dependence and the general order of magnitude: it is well known empirically[3] that the cross section for excitation of the vibration is rather small.

It is clear that one would expect the C-results to be greater than the Q-results. Superficially it seems strange that the C- and Q-results differ most at the lowest energies, but this feature can be understood by recalling that a measure of the difference between C- and Q- results is given by $k_o - k_f$, which of course decreases with increasing energy.

Table II. The total cross section.

E_o	$(10^{-3}\ e^2 / a_o)$ $\times$	20	20.27	30	40	60	80
σ_C''	$(10^{-18}\ cm^2)$	0	2.5	10.8	7.0	2.7	2.0
σ_Q''	$(10^{-18}\ cm^2)$	0	.03	6.1	4.9	2.6	1.95
σ_Q''	has its maximum for ℓ =		4	15	23	24	22
σ_Q''	is essentially zero for ℓ >		6	30	47	67	75
λ_f/d	(expression (2))		.18	.03	.02	.015	.012
$\delta pR/\hbar$	(expression (4)) evaluated at r = d		0.5	.08	.06	.04	.03
	evaluated at r corresponding to the value of ℓ that maximizes $\sigma_Q''(\ell)$		.02	0.5	0.9	1.4	1.8

N.B. (i) $E_o = 20.27 \times 10^{-3}\ e^2/a_o$ is too close to the threshold for the present method to yield reliable results, on account of the small number of phases that contribute.

(ii) There are considerable differences in the value of the expression (4), $\delta pR/\hbar$, depending on just how one evaluates δp, or V'. As a third alternative one might substitute the expectation value of the momentum transfer for δp; this yields values ~ 0.3 for the expression (4).

The basic point is that expression (4) is of the order unity but somewhat smaller so that one would expect the result for σ'' which lies somewhere between the C- and the Q- results.

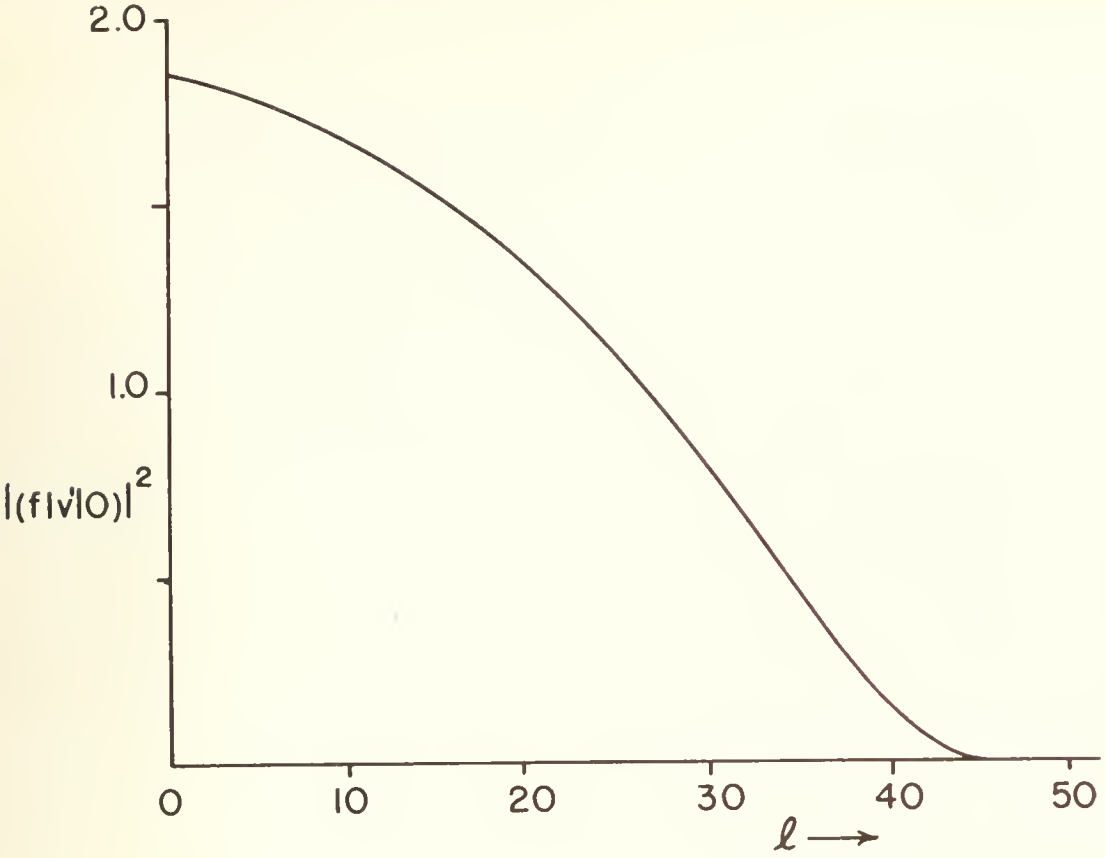


Figure 2a. The square of the transition matrix element, $|(f|V'|0)|^2$, as a function of ℓ.

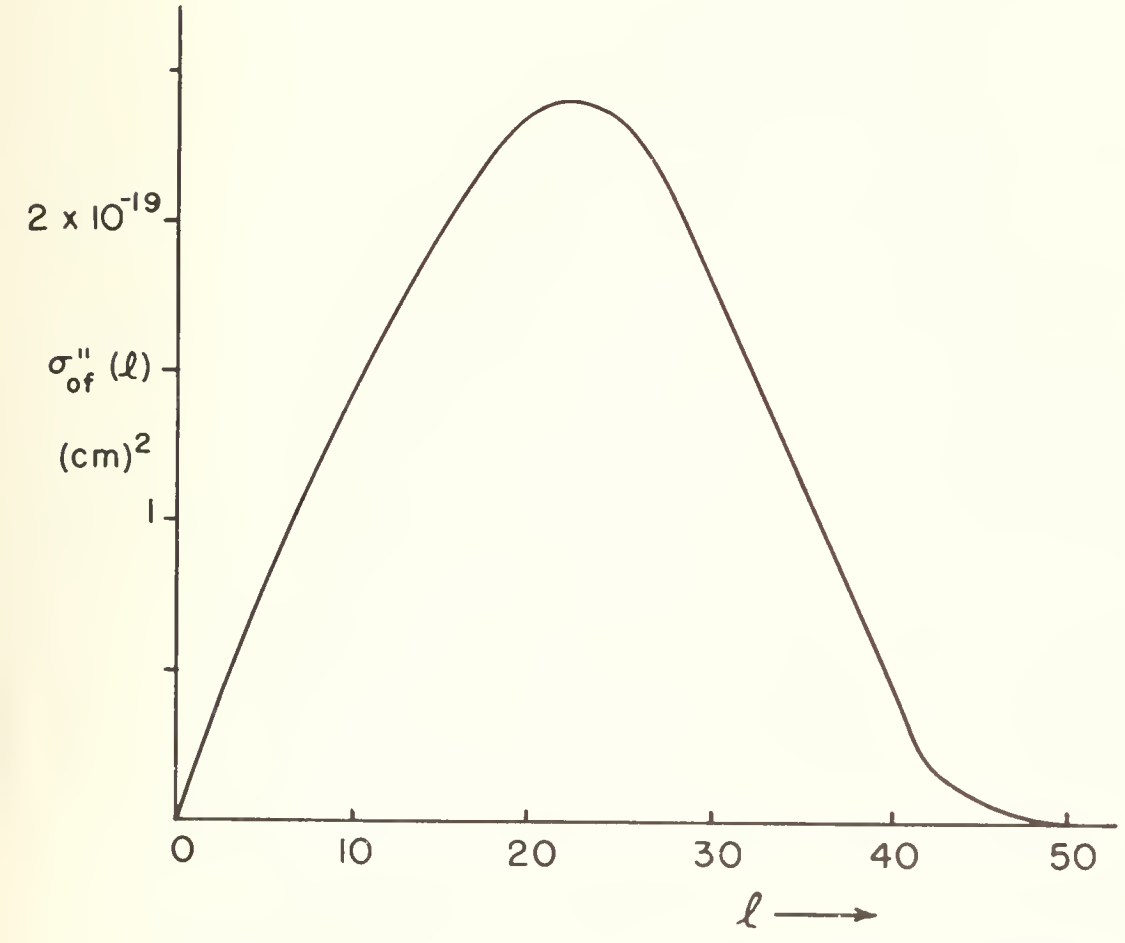


Figure 2b. The partial cross section $\sigma''_{of}(\ell)$ as a function of ℓ.

Figure 2. Dependence of the partial cross section on the angular momentum $\ell = kb$: Q-approximation, $E_o = 40 \times 10^{-3}\ e^2/a_o$.

A more detailed discussion of some features of the present method, and its relation to previous calculations, is given in Appendix B. The present method of calculation is free from some of the objections that can be raised against the previous, essentially one-dimensional calculations[4]-[6]. It is planned to investigate the approximations made here, by actually calculating higher terms, and ultimately to recalculate the cross sections for several related processes.

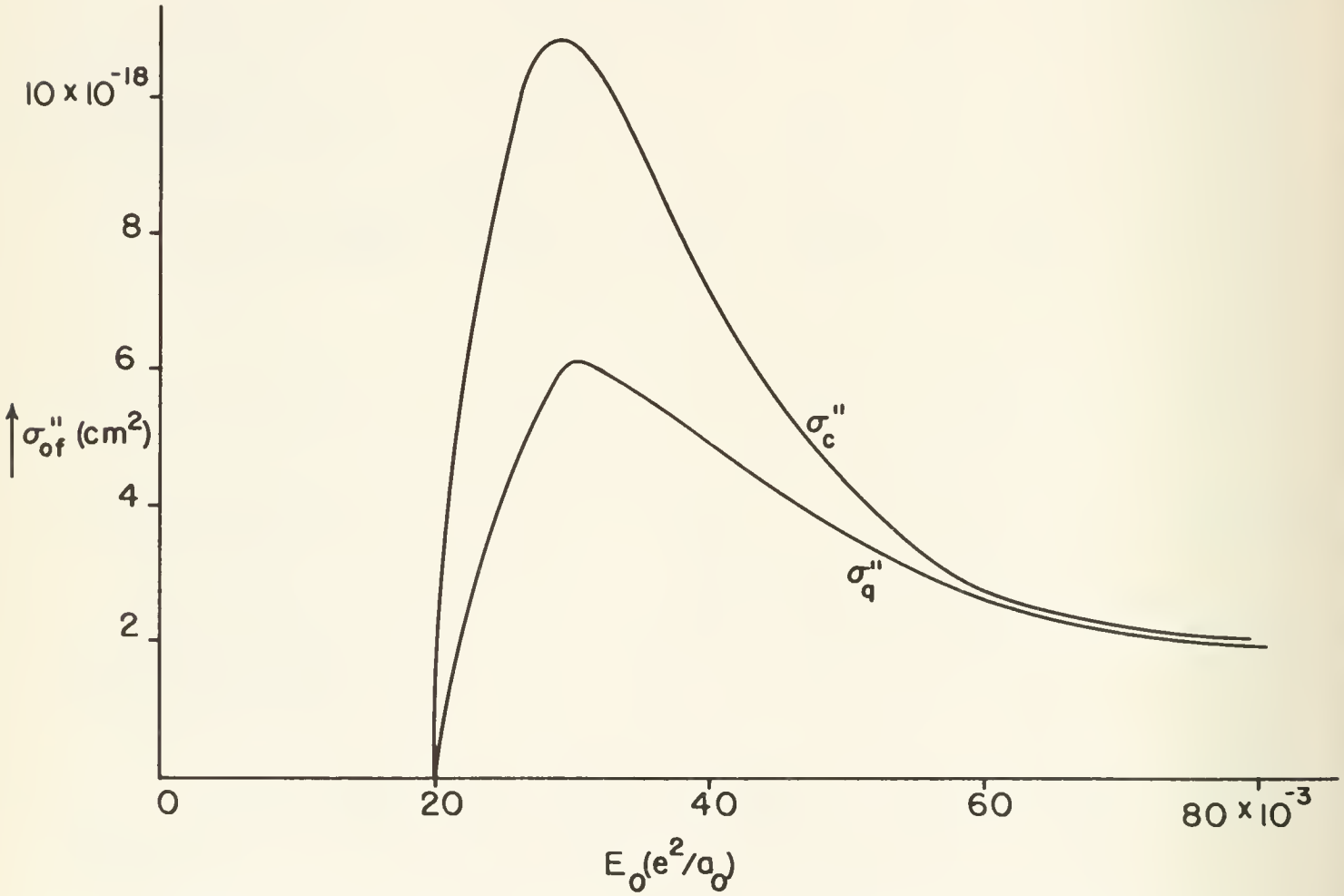


Figure 3. The total cross section σ''_{of} as a function of energy, in the C- and Q-approximations.

Acknowledgements

I should like to thank Dr. A.B. Bhatia; Prof. J.B. Keller, and Dr. Ta-You Wu for numerous discussions.

Appendix A. Normalization of the translational wave function $\chi_j(\underline{r})$.

The χ_j are continuous spectrum wave functions of energy E_j. Conventionally they are separated into a set of wave functions orthogonal with respect to energy and angular momentum. We wish to do the same for our WKB functions, replacing the angular momentum quantum number ℓ by the impact parameter b.

The b-normalization is intuitively obvious because wave functions with different b do not overlap much: the χ-function follows a well-defined classic orbit with a width $\delta b \sim 1/k$ (corresponding to $\delta \ell \sim 1$), and is essentially zero outside this. The situation is sketched in Fig. 4. We shall take χ as a function of rectangular rather than Gaussian or similar profile, so that it is finite and constant within the width δb of the orbit, and zero outside.

To prove that orthogonal functions are in fact obtained in this way, it is necessary to assume

(i) that using a rectangular profile for χ does not have any serious effects; and

(ii) that the region of overlap, G, of Fig. 3, does not contribute significantly to $\int d^3\underline{r}\ \chi^*(E,b)\,\chi(E,b')$. This latter assumption is indeed valid, since at most $\int_G d^3\underline{r}\ \cdots$ is finite, and hence it is negligible compared with $\int d^3\underline{r}\ |\chi(E,b)|^2$, which is infinite.

Energy normalization is now achieved in the conventional manner. We require

$$\int d^3\underline{r}\ \chi^*(E,b)\,\chi(E',b) = \delta(E - E'), \tag{A.1}$$

so that, using the present assumption about the rectangular profile of $\chi_j(\underline{r})$, we have

$$2\pi\, b_j\, \delta b_j \int d\underline{x}_j\ \chi^*(E,b_j)\chi(E',b_j) = \delta(E - E'), \tag{A.2}$$

where the integration extends along the classical j-orbit.

It follows from the above discussion that in the WKB approximation of equation (26) we are led to the result (31) for $|A_j(\underline{r})|^2$.

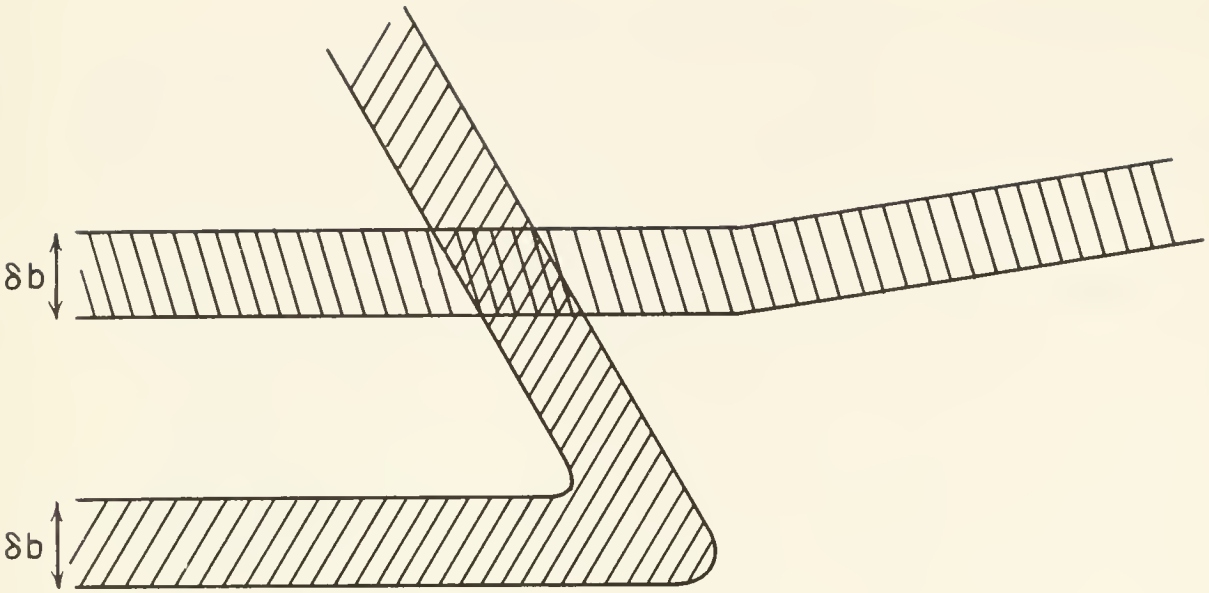
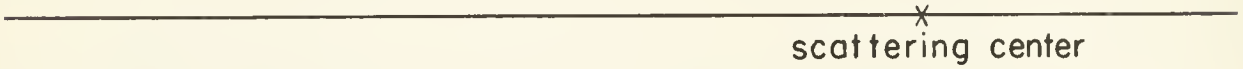


Figure 4a



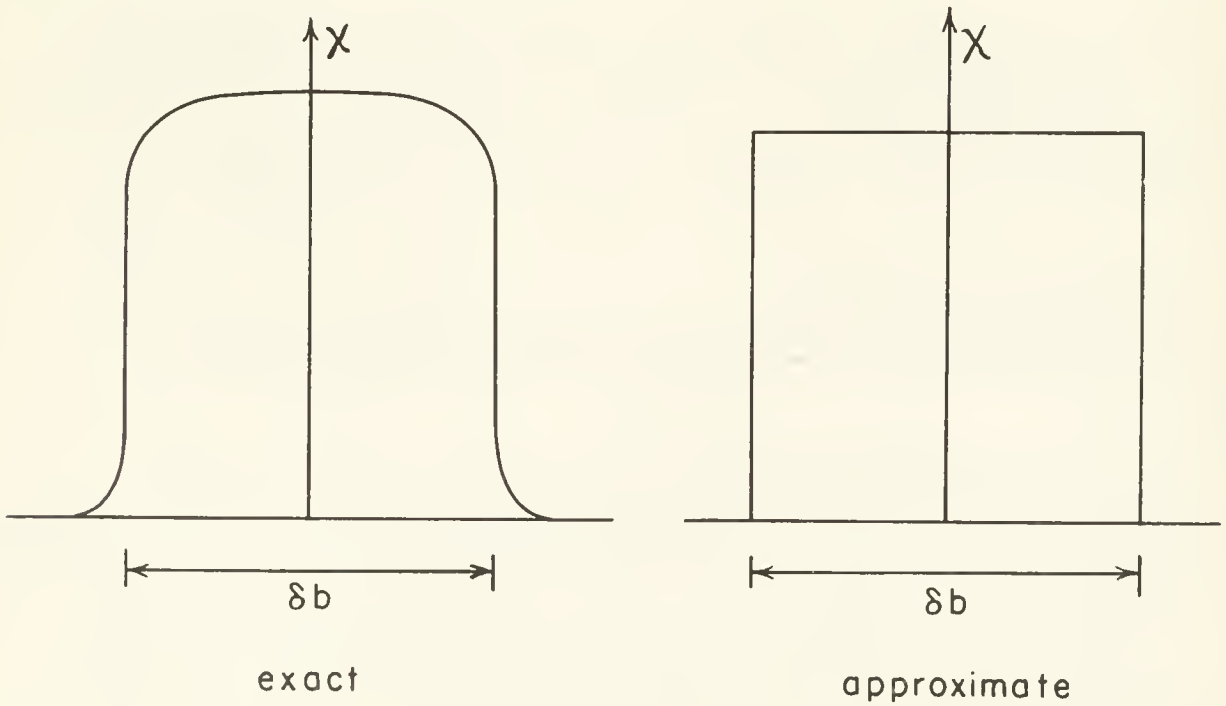


Figure 4b

Figure 4. Normalization of the translational wave function χ.
4a: Orthogonality; 4b: The profile of χ.

Appendix B. Discussion of the present method of calculation, and its relation to previous work.

We have treated two limiting cases, here labeled C and Q. Case C is the analog of a calculation of B. Widom and S.H. Bauer[7]: it is appropriate to the case where relation (2) holds and the expression (4) is very much greater than unity. The latter condition is not satisfied here, so that the phase of the wave function has to be taken into account. An attempt to do this has been made with the case Q, but it should be stated that while our treatment of case C is adequate as far as it goes, we have, in dealing with case Q, at least with its actual application to equation (38), made an underlying assumption regarding the behavior of WKB wave functions near a turning point which involves some unsolved mathematical problems.

A useful feature of the present method is that it is in principle possible to take into account non-central characteristics of V_e^o and of V', because such characteristics would not involve difficulty with the classical orbits. This is - at least formally - a characteristic advantage of the impact-parameter method over the usual formulation. So far no calculations have been made with non-central potentials and none are contemplated at this time.

In Fig. 2 are displayed the dependences on angular momentum $\ell = k_f b_f$ of the partial cross section $\sigma''_{of}(\ell) \sim (b_f/k_f)\ (f|V'|0)^2$, and also of the square of the transition matrix element $|(f|V'|0)|^2$, for a typical value of the energy ($E_o = 40 \times 10^{-3}\ e^2/a_o$). These results show how the scattering for various values of σ''_{of}. [These contributions are essentially the areas under the curves of $\sigma''_{of}(\ell)$ vs. ℓ.] One sees clearly the unsatisfactory character of previous one-dimensional calculations[4]-[6], which ascribe the total scattering to the S-wave scattering alone.

A number of recent publications [7],[8] have used the concept of an impact parameter. Of these, Takayanagi's ingenious method [8] of taking into account higher-order phases by merely modifying the wave number presents probably the first real effort in this field to take into account the three-dimensional character of the translational motion. It does seem, however, that the present method of using the

WKB approximation perhaps brings out the physical situation rather more clearly, in that the "classical" orbit and the "non-classical" phase corresponding to conditions (2) and (4) are exhibited separately.

Most previous calculations [4],[7],[8] have used a perturbation potential of the form e^{-ar}. This is very objectionable from the point of view of numerical evaluation, because most of the contribution to the matrix element comes from a region near the turning point of the classical motion, and in practice it is just here that the "actual" van der Waals potential differs most from a simple exponential repulsion. This is a difficult matter: the low energies involved mean that we should like to know $V_e(r)$ to within energies of the order 0.01 ev, so that uncertainties in the potential that are unavoidable in the present state of development may conceivably lead to significant effects.

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Errata

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The value of the normalization constant $A_j(\underline{r})$ in equation (31) is too large by a factor 2. Thus (31) should read

$$(31') \quad \left|A_j(\underline{r})\right|^2 = \begin{cases} M_e \Big/ \left\{2\hbar^2\pi\, q_j(\underline{r})\, 2\pi\, b_j \delta b_j\right\} & \text{along the classical orbit } (b_j \pm \tfrac{1}{2}\delta b_j) \\ 0 & \text{off the orbit} \end{cases}$$

The numerical values of cross-sections quoted in Table II, rows 2 and 3 (σ_Q'') are thus too large by a factor $2^4 = 16$, and so are the values of $\sigma''_{of}(\chi)$ of Fig. 2b, and σ''_{of} of Fig. 3.

(This correction does not affect any of the basic conclusions).